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Increases in solar conversion efficiencies of the ZrO₂ nanofiber-doped TiO₂ photoelectrode for dye-sensitized solar cells

Jiao Wang¹, En Mei Jin¹, Ju-Young Park², Wan Lin Wang¹, Xing Guan Zhao¹ and Hal-Bon Gu^{1*}**Abstract**

In this paper, in order to improve the efficiency of dye-sensitized solar cells, we introduced zirconia [ZrO₂] nanofibers into a mesoporous titania [TiO₂] photoelectrode. The photoelectrode consists of a few weight percent of ZrO₂ nanofibers and a mesoporous TiO₂ powder. The mixed ZrO₂ nanofibers and the mesoporous TiO₂ powder possessed a larger surface area than the corresponding mesoporous TiO₂ powder. The optimum ratio of the ZrO₂ nanofiber was 5 wt.%. The 5 wt.% ZrO₂-mixed device could get a short-circuit photocurrent density of 15.9 mA/cm², an open-circuit photovoltage of 0.69 V, a fill factor of 0.60, and a light-to-electricity conversion efficiency of 6.5% under irradiation of AM 1.5 (100 mW/cm²).

Keywords: zirconia nanofiber, titania, DSSC

Introduction

Dye-sensitized solar cells [DSSCs] have generated a considerable research interest because of their high-energy conversion efficiency (approximately 11%) and low production costs [1-3]. A typical DSSC device contains a light-harvesting layer on a photoelectrode and a Pt-coated layer on a counter electrode; both electrodes are made of a transparent conducting oxide substrate; an iodine-based electrolyte fills the space between the photoelectrode and the counter electrode to serve as a redox mediator in a sandwich-type structure. Performance of the DSSC depends on many factors such as the TiO₂ surface morphology, particle size, thickness of the photoelectrode, nature of the dye, etc. [4-10].

A high light-to-electricity conversion efficiency results from a large surface area of the mesoporous TiO₂ photoelectrode, on which the dyes can be sufficiently adsorbed. In this study, we introduced zirconia [ZrO₂] nanofibers into the mesoporous titania [TiO₂] photoelectrode. The ZrO₂ nanofibers are prepared by electrospinning. The TiO₂ film composite with ZrO₂ nanofibers creates a larger surface area than the single

TiO₂ film, in which case the amount of dye loading was increased and short-circuit photocurrent density and solar conversion efficiency are also increased.

Experimental details

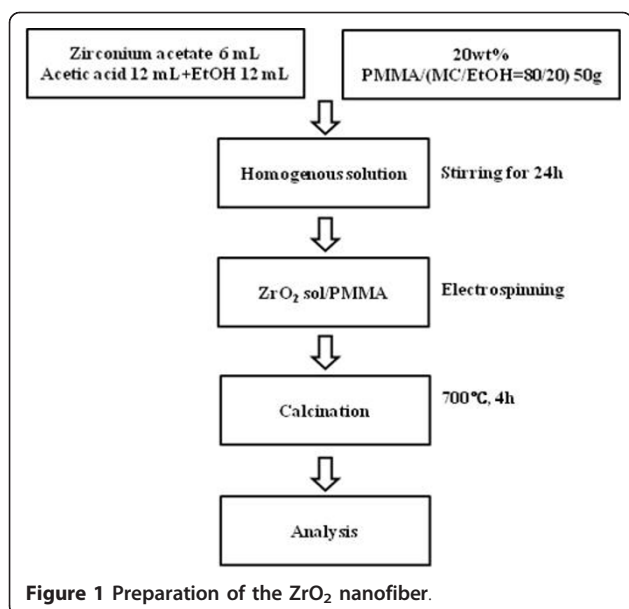
The ZrO₂ nanofiber additives were prepared by electrospinning method. At first, mixed together, 6 ml zirconium acetate, 12 ml acetic acid, 12 ml ethanol, and 50 g poly(methyl methacrylate) were stirred for 24 h; then, the compounds were sintered at 700°C for 4 h. A detailed process is displayed in Figure 1.

The TiO₂ paste was prepared by mixing TiO₂ with Degussa P-25, polyethylene glycol, acetyl acetone, distilled water, triton X-100, HNO₃, and ZrO₂ nanofibers. The concentrations of ZrO₂ nanofibers were 0, 3, 5, and 7 wt.%. The mixed solutions were ball milled at 100 rpm for 10 h. The photoelectrode was fabricated using a clean fluorine-doped tin dioxide [FTO] (approximately 8 Ω/cm², Pilkington conductive glass, Seoul, South Korea) by squeeze printing. The coated photoelectrode was heat treated at 450°C for 30 min with a heating rate of 5°C/min. The obtained photoelectrode was immersed into the ethanol solution containing [*cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium)] (N719 dye, Solaronix, Aubonne, Switzerland) for 24 h. The active area of the

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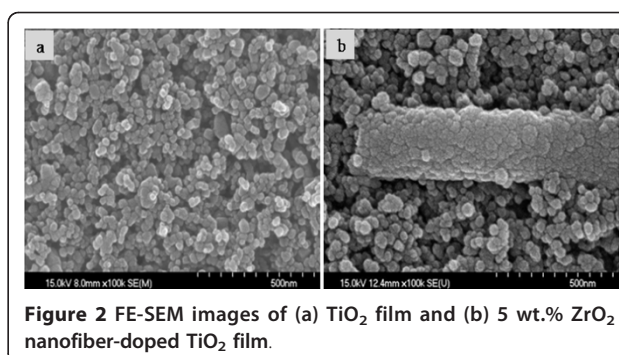
photoelectrode was $0.5 \times 0.5 \text{ cm}^2$. On the other hand, the counter electrode was prepared similar to the photoelectrode preparation. Pt-Sol (Pt catalyst/SP, Solaronix) was coated onto the FTO glass by the squeeze printing method. The coated paste was heat treated at 450°C for 30 min with a heating rate of $5^\circ\text{C}/\text{min}$.

The electrolyte solution consisted of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.5 M Li(I), 0.05 M I₂, and 0.5 M 4-t-butylpyridine in 3-methoxypropionitrile between the two electrodes. The dye-coated photoelectrode and the Pt-coated counter electrode were sandwiched using a 60- μm -thick hot-melt sealing foil (SX 1170-60, Solaronix).

The field-emission scanning electron microscope [FE-SEM] (S-4700, Hitachi, Seoul, South Korea) and BET were used to examine the morphology and the pore distribution volume of the TiO₂ film. In order to investigate the physical and optical characteristics of the dye-adsorbed TiO₂ films, the UV-visible [UV-Vis] spectrum measurement was performed. The photovoltaic properties were investigated by measuring the photocurrent-voltage characteristics under illumination with air mass [AM] 1.5 ($100 \text{ mW}/\text{cm}^2$) simulated sunlight.

Results and discussion

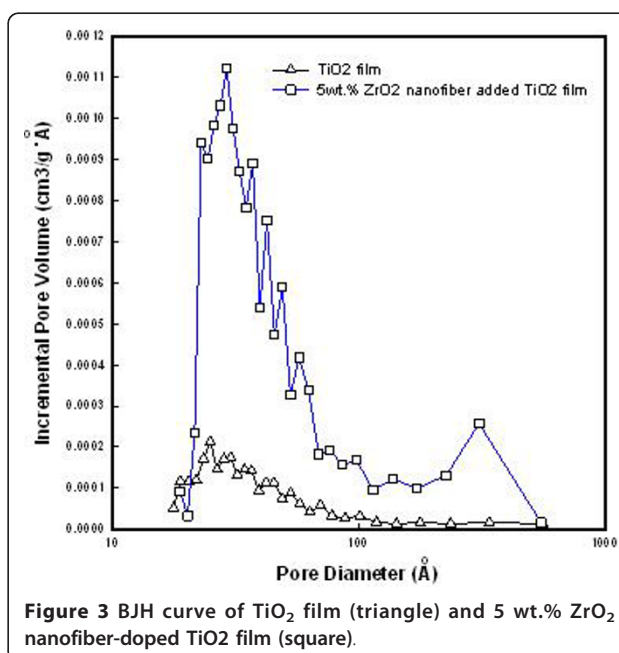
Figure 2 shows the FE-SEM images of the TiO₂ film's surface and the 5 wt.% ZrO₂ nanofiber-added TiO₂ film's surface. In the ZrO₂ nanofiber-added TiO₂ film in Figure 2b, the ZrO₂ nanofiber was shown at the surface of the TiO₂ film, or the TiO₂ film was studded with the ZrO₂ nanofiber. The TiO₂ film's surface area was increased, and the dye adsorption contents became larger by the addition of the ZrO₂ nanofiber. So, we can

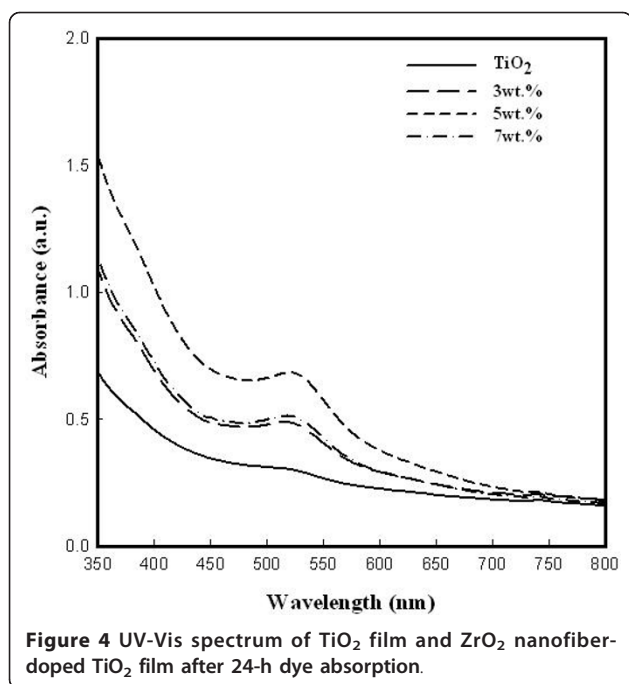


forecast that the TiO₂ electrode is able to obtain high conversion efficiency.

Figure 3 shows the pore distributions calculated from adsorption data using the Barrett-Joyner-Halenda [BJH] method. As shown in Figure 3, a broad peak was found at around 25 nm, and an added 5 wt.% ZrO₂ nanofiber at around 30 nm was observed. Compared to the pure TiO₂ film, the 5 wt.% ZrO₂ nanofiber-added TiO₂ films show a significant change in the pore size distribution. A large pore volume in BJH was observed on the TiO₂ film with 5 wt.% ZrO₂ nanofibers, which is in agreement with the results of the FE-SEM image.

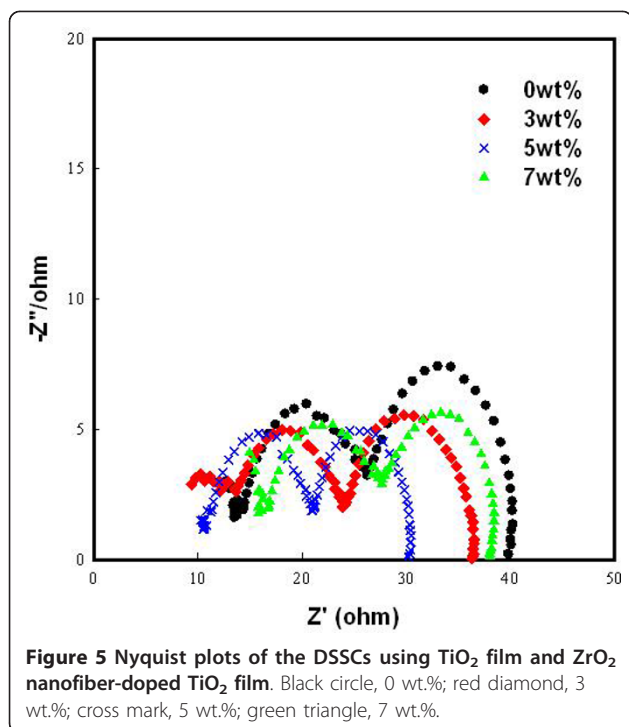
Figure 4 shows the UV-Vis absorption spectra of the dye-adsorbed TiO₂ film and the 3, 5, and 7 wt.% ZrO₂ nanofiber-doped TiO₂ films. From the results, the absorption spectra increased at around 538 nm with added ZrO₂ nanofibers doped in the TiO₂ film and also enhanced the amount of dye loading. So, the 5 wt.% ZrO₂ nanofiber-doped TiO₂ film had the best dye





loading, and also, its solar conversion efficiency was the best among the samples.

In order to determine the factors that influence the stability of the DSSCs, electrochemical impedance spectroscopy [EIS] was performed. Figure 5 shows that the Nyquist plot of EIS of the DSSCs exhibits semicircles, which are assigned to the electrochemical reaction at



the Pt counter electrode, the charge transfer at the TiO₂/dye/electrolyte interface, and the Warburg diffusion process of I⁻/I₃⁻ [9,10]. As shown in Figure 5, the second semicircle is the resistance (R_2) related to the electron transport in the TiO₂/dye/electrolyte interface which is reduced. It can be seen that the TiO₂ film and the 3, 5, and 7 wt.% ZrO₂ nanofiber-doped TiO₂ films are 13.2, 10.3, 9.6, and 11.9 Ω , respectively.

Figure 6 shows photocurrent-voltage characteristics of the DSSCs with the ZrO₂ nanofiber-doped TiO₂ film. The open-circuit photovoltage was almost the same, and the short-circuit photocurrent density increased with the added amount of ZrO₂ nanofibers and had reached the maximum at 5 wt.% of ZrO₂ nanofiber (15.9 mA/cm²). The open-circuit photovoltage [V_{oc}], the short-circuit photocurrent density [J_{sc}], the fill factor [FF], and the light-to-electricity conversion efficiency [η] at 5 wt.% added ZrO₂ nanofiber were 0.69 V, 15.9 mA/cm², 0.60, and 6.5%, respectively, as shown in Table 1. From the results, we can realize that the insertion of ZrO₂ nanofibers creates a larger surface area and reduces the resistance of the photoelectrode, especially for the optimal amount of ZrO₂ contents (7 wt.%) of the photoelectrode in DSSCs.

Conclusions

In summary, a ZrO₂ nanofiber-doped TiO₂ film was used as a photoelectrode in DSSCs. The ZrO₂ nanofiber-doped TiO₂ films had a larger surface area than the pure TiO₂ film, in which case the amount of dye loading was increased, and J_{sc} and η were also increased. The

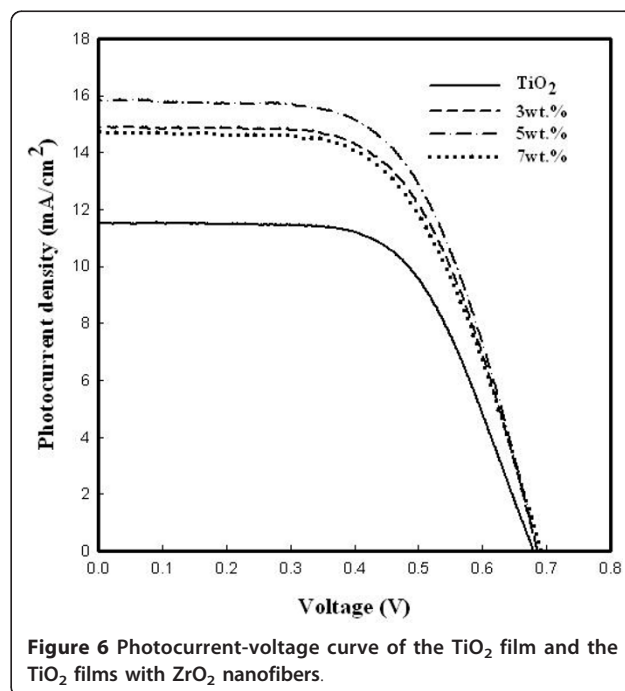


Table 1 Photocurrent-voltage characteristics of DSSCs using TiO₂ with different amounts of ZrO₂ nanofibers

| Sample | V _{oc} (V) | J _{sc} (mA/cm ²) | FF | η (%) |
|----------------------------------------------------------|---------------------|---------------------------------------|------|-------|
| Pure TiO ₂ | 0.68 | 11.5 | 0.62 | 4.9 |
| 3 wt.% ZrO ₂ nanofiber-doped TiO ₂ | 0.69 | 14.9 | 0.60 | 6.2 |
| 5 wt.% ZrO ₂ nanofiber-doped TiO ₂ | 0.69 | 15.9 | 0.60 | 6.5 |
| 7 wt.% ZrO ₂ nanofiber-doped TiO ₂ | 0.69 | 14.7 | 0.59 | 6.0 |

V_{oc}, open-circuit photovoltage; J_{sc}, short-circuit photocurrent density; FF, fill factor; η, light-to-electricity conversion efficiency; TiO₂, titania; ZrO₂, zirconia.

optimum ratio of the ZrO₂ nanofiber was 5 wt.%. The DSSC with the 5 wt.% ZrO₂ nanofiber photoelectrode provided the highest η of 6.5%, J_{sc} of 15.9 mA/cm², V_{oc} of 0.69 V, and FF of 0.60 under AM 1.5 (100 mW/cm²) simulated sunlight illumination. Therefore, ZrO₂ fibers are a promising additive for the realization of high-efficiency DSSCs.

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Authors' contributions

JW fabricated the DSSCs and UV-Vis analysis. EMJ was the paper chaser and performed the analysis of photocurrent-voltage characteristics and impedance. WLW performed the BET analysis. J-YP prepared the ZrO₂ nanofibers. XGZ performed the FE-SEM analysis. H-BG was thesis director. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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